

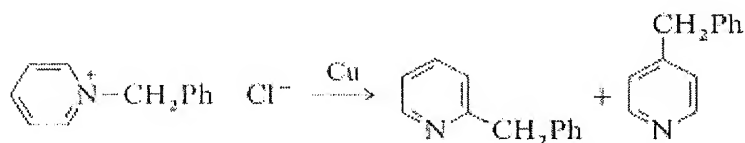
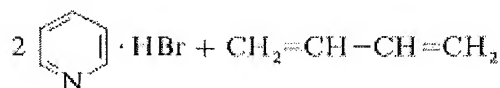
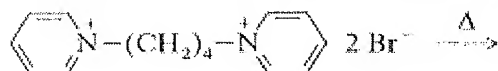
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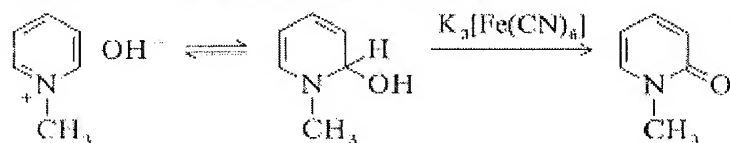
### 3.3. Quaternary Pyridinium Salts

**Properties.** Pyridine and some of its derivatives are readily converted to quaternary salts by alkylating agents such as alkyl halides. Quaternary salts can be regarded as being formed by the neutralization of strong bases (i.e., pyridinium hydroxides) with strong acids (e.g., hydrogen halides). Therefore, these salts are practically neutral when dissolved in water. Although stable under normal conditions, they are degraded into pyridine hydrohalides and alkenes on intense heating [78], or they undergo the Ladenburg rearrangement in the presence of copper as a catalyst [79]:



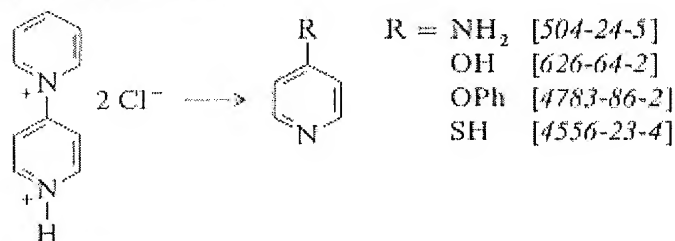
The pyridine ring of these salts is susceptible to nucleophilic attack as a result of the quaternization of the nitrogen atom. The reaction of 1-methylpyridinium salts with alkaline ferricyanide

gives *N*-methylpyridone via oxidation of a pseudobase, which is considered to exist at low concentration in equilibrium with the pyridinium hydroxide [80], [81]:



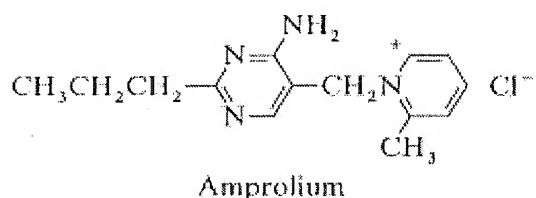
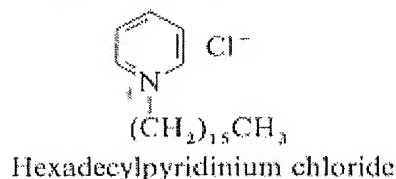
1-Pyridylpyridinium dichloride [5421-92-1], obtained from pyridine and thionyl chloride or chlorine, is particularly useful as a synthetic intermediate [82], [83]. It affords 4-amino- and 4-hydroxypyridine on ammonolysis and hydrolysis, respectively.

Treatment with phenol and sodium phenoxide gives 4-phenoxy-pyridine, and reaction with hydrogen sulfide in pyridine gives 4-mercaptopyridine [84][85] [86][87].

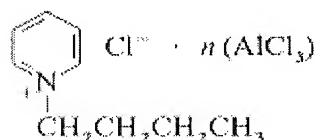


**Uses.** The major use of quaternary pyridinium salts is in the manufacture of the herbicides paraquat and diquat. These compounds are produced by the quaternization of 4,4'-bipyridyl and 2,2'-bipyridyl with methyl chloride and dibromoethane, respectively. Higher alkylpyridinium salts are used in the textile industry as dye auxiliaries and spin bath additives (antistatic agents and softeners). The higher alkylpyridinium salts also exhibit antimicrobial activity. Hexadecylpyridinium chloride

[123-03-5] is a topical antiseptic, and amprolium [121-25-5], a quaternary salt of 2-methylpyridine, is a veterinary coccidiostat.



Of the many quaternary salts, 1-butylpyridinium bromide [1124-64-7] and other lower 1-alkyl homologues are of current interest. Although each component is solid at ambient temperature, the mixture of these salts with aluminum chloride leads to melts that can exist as liquids below room temperature in fairly wide proportions.



The molten salt with  $n=2$  exhibits a specific conductivity of ca. 7 mS/cm at 25 °C [88]. The utilization of these molten salts for battery electrolytes [89] and electroplating baths for aluminum has been proposed [90]. These binary salts are reportedly excellent solvents and catalysts for Friedel-Crafts reactions [91] and for the formylation of toluene by carbon monoxide [92].

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